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(54) Optical waveguides derived from a combination of poly(perfluorocyclobutanes) and polymeric cyanates

(57) The present invention is directed to optical systems, e.g. wave guide systems, comprising at least (a) a first material which is a poly(perfluorocyclobutane), and in direct contact to this material (b) a second material which is a polycyanate resin. Preferably, both the first and the second materials are in the form of a thin layer, the layers directly adhered to each other. If the system is a wave guide system, either the waveguide can be made from the first material and at least one of the buffer layer and the cladding layer can be made from the second material, or vice versa. In a preferred embodiment, the second material is a polymer of an organic polyfunctional cyanate which is at least partly or fully fluorinated, or a copolymer comprising at least one of the said organic polyfunctional cyanates, optionally in mixture with other components.

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Description

[0001] The present invention is directed to optical elements or systems made of plastics and specifically to waveguide structures prepared from organic (co-)polymeric cyanates and poly(perfluorocyclobutanes).

[0002] Organic polymers are increasingly interesting materials in the optical or microoptical field, in integrated optics or in microsystem techniques. In these fields, they may be used in optical instruments and apparatuses or parts thereof as well as in special optics as lenses, prisms, for fixation of optical systems, as support materials for optical layers and as translucent coating materials for mirrors or lenses. Organic polymers may be used in optical fibres and for the preparation of waveguide structures. Their technical handling is relatively easy, and their density is lower in comparison to glass.

[0003] Specifically, if such plastics or organic polymers are to be used as a waveguide, a variety of requirements are to be met. The refractive index of the material should be variable in a range as broad as possible and should be adaptable to that of specific substrates. If used in the optical communication engineering, low absorptions of the materials are required at 1.3 and 1.55µm. The loss due to attenuation caused by volume defects (non-homogenities, microbubbles, microfissures) should be minimized. Besides specific technological requirements, e.g. preparation of layers and structurability, specific provisions for the use of organic polymers as waveguide structures in integrated optics are the thermal and thermo-mechanical stability, adapted extension coefficients and long term stability of optical properties.

[0004] Until now, polymethacrylates and polycarbonates have been mainly used for optical purposes. Both classes of polymers have an excellent light transmittance, but their thermal and thermo-mechanical stability is not sufficient due to their chemical structure. Thus, polymethacrylates and polycarbonates cannot practically be used at temperatures exceeding 130°C which is due to their relatively low glass transition temperatures. In addition, both types of polymers are linear, un-crosslinked polymers. This has the adverse effect that they are partly solubilized in case multilayer-systems are prepared via the application of dissolved components, e.g. by spin-coating each layer. Consequently, the layer structures as obtained are not sufficiently delimitated and neat which, however, is an essential for the preparation of waveguide structures.

[0005] There are other high performance polymers which have glass transition temperatures of more than 180°C. Examples are polyarylethersulfones, polyarylsulfones, polyaryletherketones, polyimides and polyetherimides, the processing of which, however, is more difficult than that of polymethacrylates and polycarbonates. Another disadvantage of these systems is the relatively high optical loss at wave lengths of 1.3 and 1.55µm, relevant in communication engineering.

[0006] Polyperfluorocyclobutanes (PFCB) are a relatively new class of high performance polymers. They have first been described by Babb and others. in US patents 5.037.917, 5.037.918, 5.037.919, and 5.159.038. Upon thermal curing they yield unsoluble cross-linked polymers which are characterized by high thermal stability. Waveguides prepared from PFCB in combination with buffer layers made of thermally grown SiO_2 have been described by Fischbeck et al., Electronic letters 33, 518 (1997). The layers prepared from PFCB showed very low optical losses at 1550 nm (minimum: 0.2 dB/cm). Polymeric waveguide systems consisting of more than one organic polymer are not described in this paper.

[0007] In addition, it is known to use polycyanurates for the preparation of optical components. US patents 5 208 892 and 5 165 959 describe the preparation of polycyanate resins made of a single monomer (either fluorinated or non-fluorinated). German Offenlegungsschrift DE 44 35 992 Al describes optical elements prepared from polycyanurate resins. The resins are made by polymerization of dicyanate or polycyanate compounds, optionally in mixture with di- or polyphenols or di- or polyglycidyl compounds. Like polyperfluorocyclobutanes, polycyanurates yield unsoluble cross-linked polymers upon thermal curing, and these polymers are as well characterized by high thermal stability. They are specifically useful due to their excellent adhesional force on a variety of substrates, for example silicon, silica or a variety of organic polymers. Refractive index and glass transition temperature of the cured cross-linked polymers may be varied in broad ranges, due to the easy availability of a great number of di- and mono-functional cyanate monomers which may be copolymerized with each other. Polycyanurates of the kind mentioned above are partly commercially available. Completely cured polycyanurates known in the art which consequently are stable for long terms may have optical losses of about 0.2 dB/cm at 1.3µm. However, the optical losses are not less than 0.5dB/cm at 1.55µm which is important in communication engineering technologies.

[0008] It is the problem of the present invention to provide optical systems, more specifically optical multi-layer systems which are thermally and thermomechanically stable for long terms, which may be easily compounded and manufactured and which have low optical losses at 1.3 and at 1.55µm. Further, the respective components or layers, respectively, of the said systems should have refractive indices which are adapted to each other as required.In addition the invention provides waveguide structures prepared from such multi-layers.

[0009] The problem of the invention has been solved by providing a combination of components or materials at least one of which has been prepared from PFCB and at least one of which has been prepared from specific polycyanate

resins (polymeric cyanates) as defined below. Combinations, especially layers of the said substances, may be combined to obtain optical structures according to the present invention. It has been found that such combinations are specifically valuable in the preparation of waveguides structures having the above mentioned desired properties.

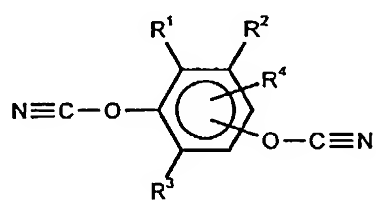
[0010] The composition of the PFCB to be used in the present invention is not critical. For example, PFCB's as described in J. Polymer Sci.: Part A: Polymer Chem., 31, 3465 (1993); 33, 1859 (1995); Macromolecules 29, 852 (1996); and J. Appl. Polym. Sci. 69, 2005 (1998) may be advantageously used. In addition, layers of PFCB's as described in the US patents of Babb and Babb et. al. as mentioned above may be incorporated into the present optical systems.

[0011] The polycyanate resins (polymeric cyanates) may be selected from those which have a rather low refractive index adapted to that of the PFCB chosen. Such polymeric cyanates may be formed by polymerization or copolymerization of organic cyanates, preferably polyfunctional cyanates, which consist of or contain at least one monomer which is partly or fully fluorinated, optionally in admixture with other cyanates or substances as defined below.

[0012] For the preparation of the said polymeric cyanates, one, two, three or even more of the said organic cyanates may be used. The expression "polyfunctional cyanate" means that at least two NCO groups are present in the molecule. However, the polyfunctional cyanate may carry even more NCO groups, for example three, four, or even up to at least 22. The NCO groups are bound to organic radicals via the oxygen atom. The polyfunctional cyanate is at least partly or is fully fluorinated. "Partly fluorinated" means that at least one fluorine atom is present in the molecule. "Fully fluorinated" means that hydrogen atoms are completely substituted by fluorine atoms. The whole molecules, or single organic radicals or groups (e.g. methyl, methylene, alkyl, aryl groups), respectively, may be fully fluorinated.

[0013] The organic structure of the (preferably polyfunctional) cyanate or cyanates is not necessarily determined; however, the following polyfunctional cyanates may preferably be selected (with the proviso that the or at least one of the cyanates chosen for (co-)polymerization carries at least one fluorine atom):

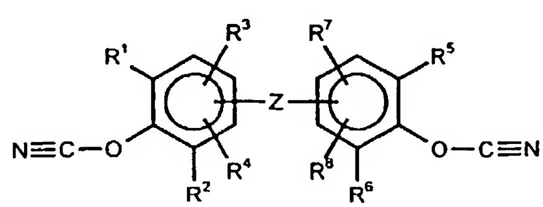
1. Difunctional cyanates of formula I:



(I)

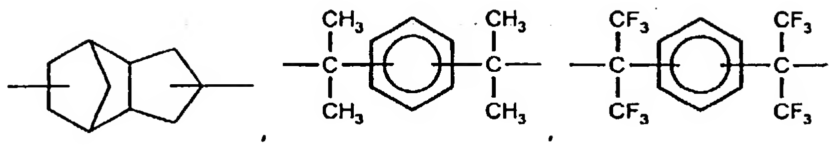
wherein R^1 to R^4 are independently from each other hydrogen, optionally substituted C_1-C_{10} alkyl, C_3-C_8 cycloalkyl, C_1-C_{10} alkoxy, halogen, phenyl or phenoxy. The alkyl or aryl groups may be unfluorinated or they may carry at least one fluorine atom. In one embodiment, at least one of the alkyl or aryl groups present in the molecule is fully fluorinated. In another embodiment, the difunctional cyanate molecule is fully fluorinated. Examples are phenylene-1,3-dicyanate, phenylene-1,4-dicyanate, 2,4,5-trifluorophenylene-1,3-dicyanate or 2,3,5-trifluorophenylene-1,4-dicyanate.

2. Difunctional cyanates of formula II:



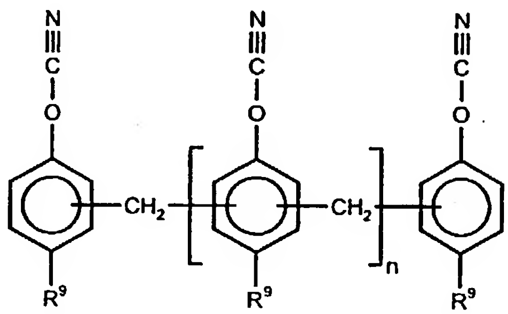
(II)

wherein R^1 to R^4 and R^5 to R^8 are defined as R^1 to R^4 above, Z is a chemical bond, SO_2, CF_2 CH_2, CHF, $CH(CH_3)$, isopropylene, hexafluoroisopropylene, n- or iso-C_1-C_{10} alkylene which may be partly or fully fluorinated, O, NR^9, N=N, CH=CH, C(O)O, CH=N, CH=N-N=CH, alkyloxyalkylene having 1 to 8 carbon atoms which is optionally partly or fully fluorinated, S, $Si(CH_3)_2$; R^9 is hydrogen or C_1-C_{10} alkyl, or



Examples are 2,2'-bis(4-cyanato-phenyl)propane, 2,2'-bis(4-cyanato-phenyl)hexafluoropropane, biphenylene-4,4'dicyanate, 2,3,5,6,2',3',5',6'octafluorobiphenylene-4,4'-dicyanate.

3. Polyfunctional cyanates of formula III:



(III)

wherein R^9 is defined as above and n is an integer of from 0 to 20.

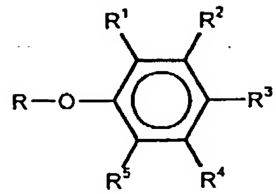
4. Dicyanates according to formula IV:

$$N{\equiv}C\text{-}O\text{-}R^{10}\text{-}O\text{-}C{\equiv}N \qquad \text{(IV)}$$

wherein R^{10} is $C(R')_2$-R"-$C(R')_2$, wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated alkyl or alkenyl group having preferably 1 to 6, more preferably 2 to 4 carbon atoms. R' is more preferred hydrogen. R" may be an non-aromatic hydrocarbon group, preferably an alkylene of 2 to 12, more preferably to 6, carbon atoms. Further, R" may have an arylenic structure. Preferably, R^{10} is a straight, branched, or cyclic non-aromatic hydrocarbon radical or a non-aromatic hydrocarbon radical comprising a cyclic structure. Preferably, the non-aromatic hydrocarbon radical has 1 to 15, more preferably 3 to 12 carbon atoms. It is to note that each of the carbon atoms of R^{10} may carry 1, 2 or, if it is a terminal carbon atom, 3 fluorine atoms. Fully fluorinated carbon atoms ($-CF_3$, $-CF_2-$) are preferred. Specific examples are: $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}O\text{-}C{\equiv}N$, $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}O\text{-}C{\equiv}N$, or $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}O\text{-}C{\equiv}N$.

[0014] In the preparation of the polymeric cyanates, the above mentioned polyfunctional cyanates may be used either alone or in mixture of two, three or even more of them.

[0015] Further, the properties of the polymeric cyanates thus obtained may be modified by incorporating one or more of the following monocyanates having formula Va or Vb:

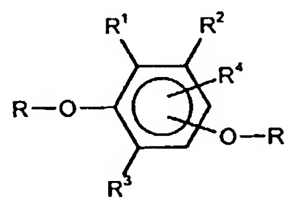


Va

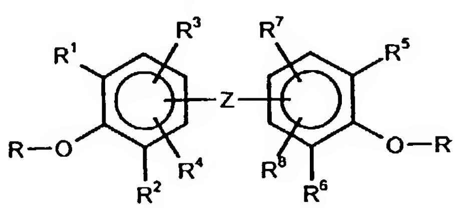
R-O-R^{11} Vb

wherein R^1 to R^5 are as previously defined for the dicyanates of formulas I and II, R is N≡C- and R^{11} is a straight, branched, or cyclic non-aromatic hydrocarbon radical or a non-aromatic hydrocarbon radical comprising a cyclic structure. Preferably, the alkyl radical has 1 to 15, more preferably 3 to 12 carbon atoms. Preferably, at least one fluorine atom is present in the monocyanate of formula Va or Vb. If fluorine atoms are present in formula Vb, R^{11} is $C(R')_2$-$CFR"_2$, wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated alkyl or alkenyl group having preferably 1 to 13, more preferably 3 to 11 carbon atoms. Each of R" may independently be defined as R'. Further, R" may have an arylic structure. It is to note that each of the carbon atoms of R may carry 1, 2 or, if it is a terminal carbon atom, 3 fluorine atoms. Fully fluorinated carbon atoms ($-CF_3$, $-CF_2$-) are preferred. Further, it is preferred that one or both of R' are hydrogen and/or one of R" is fluorine or a partly or fully fluorinated alkyl and the other is a partly or, more preferable, fully fluorinated alkyl which may be straight, branched or cyclic. Specific examples for the cyanates of formula Vb are $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF_3$, $N{\equiv}C\text{-}O\text{-}CH_2\text{-}C(CF_3)_2F$, $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CHF\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $N{\equiv}C\text{-}O\text{-}CH_2\text{-}CF_2\text{-}CF{=}CF\text{-}CF_2\text{-}CF_2\text{-}CF_3$. Specific examples for formula Va are phenylcyanate, 4-bromophenylcyanate, perfluorophenylcyanate, 3-trifluoromethylphenylcyanate.

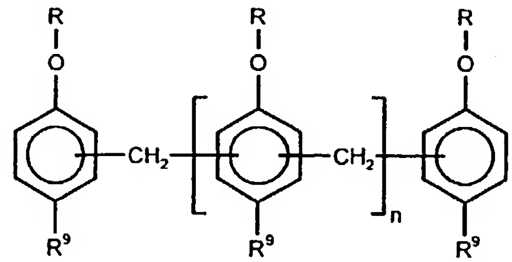
[0016] Alternatively or in addition, the properties of the polymeric cyanates thus obtained may be modified by incorporating one or more phenols having either formula Va above or formulas Vc, Vd or Ve:



Vc



Vd



Ve

wherein Z and R^1 to R^9 are as defined above for the dicyanates of formulas I and II, but wherein R is hydrogen. The phenols may, but must not necessarily, be partly or fully fluorinated.

[0017] Examples are 2,2-bis(4-hydroxyphenyl)propane, 2,2-bis(4-hydroxyphenyl)hexafluoropropane, biphenylene-4,4'-diphenol, 2,3,5,6,2',3',5',6'-octafluorobiphenylene-4,4'diphenol.

[0018] Alternatively or in addition, the properties of the polymeric cyanates thus obtained may be modified by incorporating one or more monoalcohols having formula Vb wherein R^{11} is as defined above, and wherein R is hydrogen. Examples are $HO\text{-}CH_2\text{-}CF_2\text{-}CF_3$, $HO\text{-}CH_2\text{-}C(CF_3)_2F$, $HO\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $HO\text{-}CH_2\text{-}CHF\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $HO\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_3$, $HO\text{-}CH_2\text{-}CF_2\text{-}CF{=}CF\text{-}CF_2\text{-}CF_2\text{-}CF_3$.

[0019] Alternatively or in addition, the properties of the polymeric cyanates thus obtained may be modified by incorporating one or more non-aromatic dihydroxy compounds having formula Vf

$$R\text{-}O\text{-}R^{10}\text{-}O\text{-}R \qquad \text{Vf}$$

wherein R^{10} is as defined for the dicyanates of formula IV above. Examples are $HO\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}OH$, $HO\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}OH$, $HO\text{-}CH_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CF_2\text{-}CH_2\text{-}OH$.

[0020] Alternatively or in addition, the properties of the polymeric cyanates thus obtained may be modified by incorporating one or more glycidethers of formulas Va to Ve wherein R is glycidyl, and R^1 to R^9, R^{11} and Z are defined as above.

[0021] Specifically, the refractive index may be influenced by these additives as desired. Thus, as detailed more specifically below, the presence of fluorine lowers the refractive index, while it is increased by the presence of bromine. In addition, by controlling the amount of glycidylic groups or the ratio of non-aromatic groups (especially of straight alkyl(ene) groups) to aromatic groups, this parameter may further be adjusted as required in order to obtain the desired refractive index difference between the cyanate polymer and the PFCB.

[0022] The polycyanate resins (polymeric cyanates) according to the invention may preferably be obtained by mixing at least one of the polyfunctional cyanates of formulas I to IV, optionally together with at least one of the monocyanates, phenols, monoalkohols, dihydroxyalkanes or aromatic or non-aromatic glycidethers of formulas Va to Vf as described above. Use of the said substances may be advantageous in order to further vary or improve the refractive index or other properties, e.g. compounding, moulding, or other optical properties.

[0023] If more than one polyfunctional cyanate is used in the preparation of the polycyanate, the ratio of the different polyfunctional cyanates may be freely chosen. Instead, the polymeric cyanates may be prepared using only one of the said polyfunctional cyanates of formulas I to IV. If additional components are present, the ratio is usually not critial. Preferably, the polyfunctional cyanates of formulas I to IV are present in a molar amount of at least 25%, more preferred of at least 50%, and specifically preferred not more than 67% related to the total amount of moles of monomers present in the mixture to be (co-)polymerized. If one or more monocyanates are added to the mixture, they are preferable present in an amount of up to 20 % or 25 % by mol per mol of monomers to be polymerized. If phenols or alcohols are present, they are preferably present in an amount of up to about 60 or 65 mol-%. If glycidethers are added, they are preferably present in an amount of up to about 60 or even about 70 mol-%. Preferably, the monomer non-cyanates are incorporated in a total amount of not more than about 65 to 70 mol-% per mol of the total monomers to be polymerized.

[0024] The starting compounds for the polymeric cyanate as described above are preferably warmed up after mixing. The temperature may be chosen as required; a range of about 120°C to 170°C is preferred. Preferably, the reaction is performed in the absence of oxygen, e.g. in a sealed vessel (under an inert gas atmosphere). The mixture is allowed to react until a liquid or viscous prepolymer (resin) is obtained. This prepolymer or resin is soluble in useful solvents, preferably in solvents having high polarity, e.g. ethylethoxyacetate or chlorobenzene. In general, the prepolymer is processed in a respective solution, e.g. by spin-coating of a solution containing 25 to 75% by weight of the prepolymer,

more preferably about 50% by weight of the prepolymer. The prepolymer solution may be applied to a suitable substrate or the like, consisting of e.g. silicon, quartz or an organic polymer, or onto a buffer layer, e.g. of PFCB. After being brought into the desired shape (e.g. into a layer of desired thickness) it is cured (e.g. at temperatures in the range of 200° to 260°C) in order to provide the desired network between the cyanate groups.

[0025] It should be clear that the term "resin" is independent of the condition of the polymeric cyanate, e.g. whether it is in a prepolymerized condition or is partly or completely cured.

[0026] The polycyanate resins according to the present invention have a glass transition temperature in the range of 100° to 300°C, and their refractive index at 1.55μm may be controlled in the desired range, specifically of from about 1.40 to about 1.60. Specifically, the more fluorinated monomers are used, or the more fluorine parts per weight are present in the mixture, related to the weight of the mixture to be polymerized, the lower is the refractive index of the polycyanate copolymer obtained. This is especially the case if fully fluorinated alkyl(ene) chains are contained in the molecule. On the other hand, use of brominated derivatives of the cyanate monomers as defined above will raise the refractive index of the copolymer obtained. Thus, monomer compounds of e.g. formula Va wherein at least one of R^1, R^2, R^3, R^4 or R^5 or of e.g. formula Vb wherein R^{10} carries at least one bromine atom and R is N≡C, may be advantageously added to the mixture. Instead or in addition, brominated polyfunctional cyanates may also be used.

[0027] The polycyanate resins according to the present invention are used for the preparation of optical systems, together with PFCB. PFCB as well as polycyanate resins may be applied in a dissolved state, e.g. by spin-coating. For example, they may be used for the preparation of waveguide structures. For such structures, PFCB may be used as a waveguide, while polycyanate resin is used as the material for buffer and/or cladding, the refractive index of the polycyanate resin being lower than that of the PFCB. Alternatively, PFCB may be used for buffer and/or cladding, while a polycyanate resin having a greater refractive index is used for the waveguide. In the preparation of such a waveguide structure, each layer applied is preferably cured (e.g. thermally) before the next, different layer is applied. For example, a first layer of either PFCB or polycyanate is spin-coated onto a suitable substrate, e.g. silicon, quartz, or an organic polymer, and is cured. If this layer shall serve as a buffer layer, the second layer serving as waveguide is made from the other material mentioned. Following curing, structurization may be performed e.g. via reactive ion etching (RIE) after this second layer has been sputtered with aluminum, and the etching mask is subsequently removed in a chemical etching bath. Last, a layer of the first material (or a material different to the first one, but having the same refractive index) is spin coated and cured, in order to provide the cladding layer.

Alternatively, any one of the layers mentioned may be substituted by another material. Such materials are known in the art (e.g. SiO_2 as buffer).

[0028] The selection of suitably matching resins for waveguide, cladding, and optionally the buffer will be easily made by a skilled person who is able to control the refractive index via the teachings given in this application. The layers show excellent adhesion to each other and to the substrate.

[0029] The invention is now further illustrated by way of examples.

Example 1

[0030] 12.9 g of a substituted dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is hexafluoroisopropyl) and 3.7 g of a partly fluorinated monocyanate (compound Vb wherein R is CN and R^{11} is CH_2-CF_2-CF_2-CF_3) are heated to 160°C in a sealed vessel for a time of four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 160°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of ethylethoxyacetate (EEA). Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4776 at 1.55 μm.

Example 2

[0031] 15.5 g of a partly fluorinated dicyanate (compound IV wherein R^{10} is CH_2-CF_2-CF_2-CF_2-CF_2-CH_2) and 3.5 g dicyanate of bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is isopropyl) are heated to 160°C in a sealed vessel for a time of about six hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 160°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which is cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4739 at 1.55 μm.

Example 3

[0032] 10.6 g of a substituted dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is hexafluoroisopropyl) 3.1 g of a partly fluorinated dicyanate (compound IV wherein R^{10} is CH_2-CF_2-CF_2-CF_2-CF_2-CH_2) and 3.0

g of a monocyanate (compound Va wherein R is CN, R^1, R^2, R^3, R^5 is H, R^3 is Br) are heated to 160°C in a sealed vessel for a time of four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 160°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4958 at 1.55 µm.

Example 4

[0033] 6.9 g of a substituted dicyanate of Bisphenol F (compound II wherein R^1, R^2, R^5, R^6 is CH_3, R^3, R^4, R^7, R^8 is H, Z is CH_2) 5.2 g of a partly fluorinated dicyanate (compound IV wherein R^{10} is CH_2-CF_2-CF_2-CF_2-CF_2-CH_2) and 3.0 g of a partly fluorinated alcohol (compound Vb wherein R is H, R^{11} is CH_2-CF_2-CF_2-CF_3) are heated to 140°C in a sealed vessel for a time of five hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 140°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4780 at 1.55 µm.

Example 5

[0034] 12.9 g of a substituted dicyanate of Bisphenol A (compound II wherein R^1-R^4 is H, R^5-R^8 is H, Z is hexafluoroisopropyl), and 3.0 g of a fully fluorinated monocyanate (compound Vb wherein R is CN, R^{11} is C-$(CF_3)_2$) are heated to 130°C in a sealed vessel for a time of four hours. The reaction is terminated before gelling starts, and a clear, pale yellow prepolymer is obtained which is viscous at 130°C and is solid at room temperature. The prepolymer is brought into solution by mixing it with 50 % by weight of EEA. Spin-coating of this solution onto a substrate made of silicon wafer yields a layer which may be cured at 240°C for one hour in a drying oven. The product has a refractive index of 1.4756 at 1.55 µm.

Example 6

[0035] A 50 weight-% solution of the prepolymer of example 1 in EEA is spin-coated onto a silicon wafer, yielding a layer of about 8 pm thickness. Curing is performed at 240°C in a drying oven for one hour. Onto this cured layer, a PVCB solution (XU 35121.41 of The Dow Chemical Company) is spin-coated, again yielding a layer of 8 µm thickness. Also, this layer is cured at 240°C in the drying oven for about 1 hour. According to known methods, an aluminum layer of about 100 nm is sputtered onto the said PFCB layer followed by its structurization by way of photolithography and chemical etching. Subsequently, the PFCB waveguides are structured by aid of oxygen RIE technique (typical rate 100 nm/min using pure oxygen), and the etching mask is removed by treatment in a chemical etching bath. Then, the upper cladding layer is applied by spin-coating another prepolymer solution as described in example 1 followed by curing at 240°C for 1 hour. Using near field technique a difference of 0.0085 of the refractive index between the waveguide and its surrounding is measured. Cut-back measurements of light intensities of waveguides of different length yielded a loss of 0.35 dB/cm at 1.55 µm.

Example 7

[0036] A 50 weight-% solution of PFCB (XU 35121.41 of The Dow Chemical Company) is spin-coated onto a silicon wafer, yielding a layer of about 8 µm thickness. Curing is performed at 240°C in a drying oven for one hour. Onto this cured layer, the prepolymer of example 3 (50 weight-% in EEA solution) is spin-coated, again yielding a layer of 8 µm thickness. Also, this layer is cured at 240°C in the drying oven for about 1 hour. According to known methods, an aluminum layer of about 100 nm is sputtered onto the said PFCB layer followed by its structurization by way of photolithography and chemical etching. Subsequently, the PFCB waveguides are structured by aid of oxygen RIE technique (typical rate 100 nm/min using pure oxygen), and the etching mask is removed by treatment in a chemical etching bath. Then, the upper cladding layer is applied by spin-coating the same PFCB solution as described above followed by curing at 240°C for 1 hour. Using near field technique a difference of 0.0096 of the refractive index between the waveguide and its surrounding is measured. Cut-back measurements of light intensities of waveguides of different lenght yielded a loss of 0.43 dB/cm at 1.55 µm.

Claims

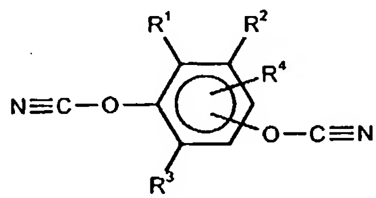
1. Optical system comprising at least (a) a first material which is a poly(perfluorocyclobutane), and in direct contact to this material (b) a second material which is a polycyanate resin.

2. Optical system according to claim 1 wherein both the first and the second materials are in the form of a thin layer, the layers directly adhered to each other.

3. Optical system according to claim 2 which is an optical waveguide system, wherein either the waveguide is made of the first material and at least one of the buffer layer and the cladding layer is made of the second material, or the waverguide is made of the second material and at least one of the buffer layer and the cladding layer is made of the first material.

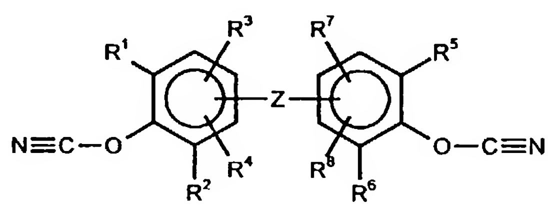
4. Optical system according to any of the preceding claims wherein the second material is a polymer of an organic polyfunctional cyanate which is at least partly or fully fluorinated, or a copolymer comprising at least one of the said organic polyfunctional cyanates, optionally in mixture with other components.

5. Optical system according to claim 4 wherein the or at least one of the polyfunctional cyanate(s) is selected from: difunctional cyanates of formula I:



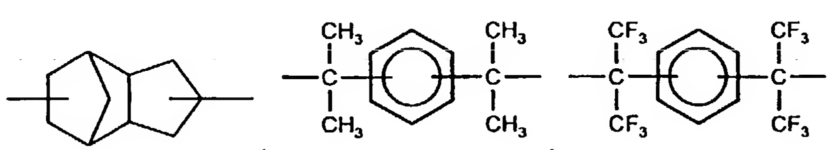
(I)

wherein R^1 to R^4 are independently from each other hydrogen, optionally substituted C_1-C_{10} alkyl, C_3-C_8cycloalkyl, C_1-C_{10} alkoxy, halogen, phenyl or phenoxy, the alkyl or aryl groups being unfluorinated, partly fluorinated or fully fluorinated, with the proviso that (I) carries at least 1 fluorine atom,
difunctional cyanates of formula II:

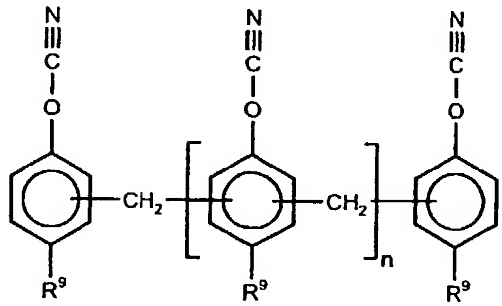


(II)

wherein R^1 to R^4 and R^5 to R^8 are defined as R^1 to R^4 above, Z is a chemical bond, SO_2, CF_2 CH_2, CHF, $CH(CH_3)$, isopropylene, hexafluoroisopropylene, n- or iso-C_1-C_{10} alkylene which may be partly or fully fluorinated, O, NR^9, N=N, CH=CH, C(O)O, CH=N, CH=N-N=CH, alkyloxyalkylene having 1 to 8 carbon atoms, S, $Si(CH_3)_2$; R^9 is hydrogen or C_1-C_{10} alkyl, or



with the proviso that (II) carries at least 1 fluorine atom, polyfunctional cyanates of formula III:



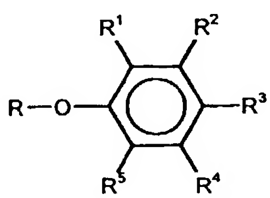
(III)

wherein R^9 is defined as above and n is an integer of from 0 to 20, with the proviso that (III) carries at least 1 fluorine atom,
and
dicyanates according to formula IV:

$$N{\equiv}C\text{-}O\text{-}R^{10}\text{-}O\text{-}C{\equiv}N \qquad (IV)$$

wherein R^{10} is $C(R')_2$-R''-$C(R')_2$, wherein each R' is, independently from the other, hydrogen or fluorine or an optionally substituted, preferably fluorinated alkyl or alkenyl group, and R" is a non-aromatic hydrocarbon group or may have an arylenic structure, with the proviso that (IV) carries at least one fluorine atom.

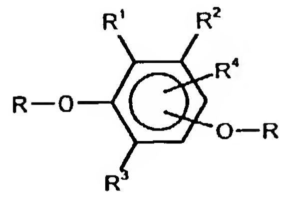
6. Optical system according to claim 4 or 5, wherein the polymer or copolymer of at least one organic polyfunctional cyanate has been prepared by copolymerizing at least one of the following compounds:
monocyanates having formula Va or Vb:



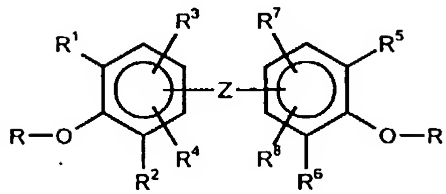
Va

$$R\text{-}O\text{-}R^{11} \qquad Vb$$

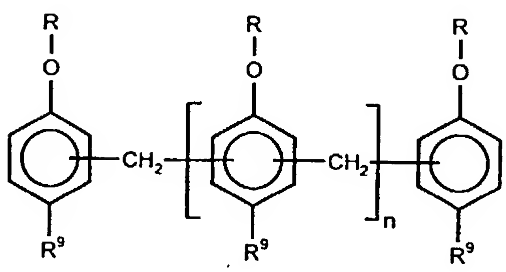
wherein R^1 to R^5 are as previously defined for the dicyanates of formulas I and II, R is N≡C- and R^{11} is a straight, branched, or cyclic non-aromatic hydrocarbon radical or a non-aromatic hydrocarbon radical comprising a cyclic structure,
phenols having either formula Va above or formulas Vc, Vd or Ve



Vc



Vd



Ve

wherein Z and R^1 to R^9 are as defined above for formulas I and II, and wherein R is hydrogen, monoalcohols having formula Vb wherein R^{11} is as defined above, and wherein R is hydrogen, non-aromatic dihydroxy compounds having formula Vf

$$R\text{-}O\text{-}R^{10}\text{-}O\text{-}R \qquad \text{Vf}$$

wherein R^{10} is as defined for the dicyanates of formula IV above,
and
glycidethers of formulas Va to Ve wherein R is glycidyl, the other radicals being as defined above, in addition to at least one polyfunctional cyanate.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 11 2597

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Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
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A	FISCHBECK G ET AL: "SINGLEMODE OPTICAL WAVEGUIDES USING A HIGH TEMPERATURE STABLE POLYMER WITH LOW LOSSES IN THE 1.55MUM RANGE" ELECTRONICS LETTERS,GB,IEE STEVENAGE, vol. 33, no. 6, page 518-519 XP000693277 ISSN: 0013-5194 * WHOLE ARTICLE *	1	
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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	26 November 1999	Depijper, R

CATEGORY OF CITED DOCUMENTS

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